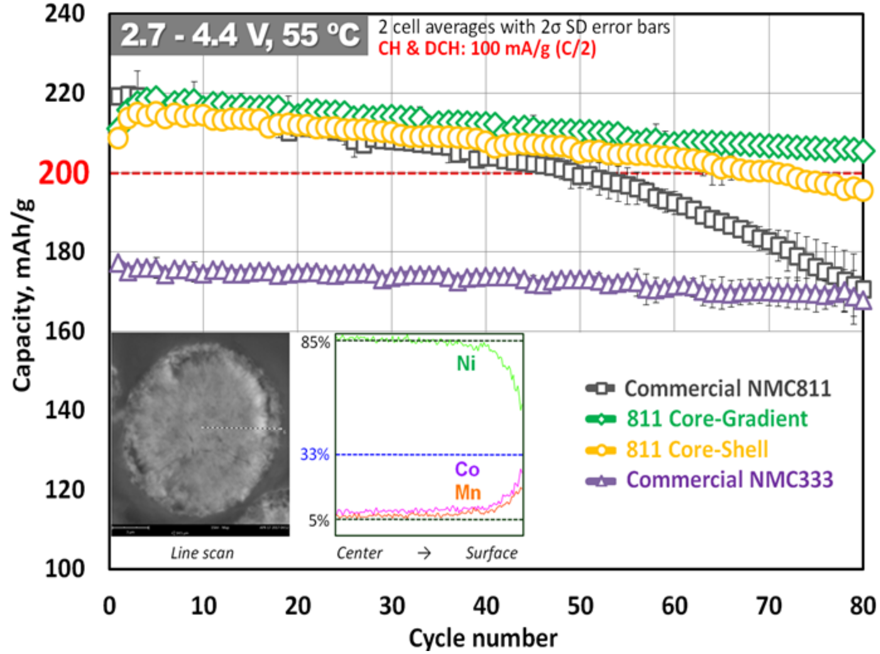

Process Development and Scale up of Advanced Active Battery Materials – Gradient Cathode Materials

Youngho Shin **Ozgenur Feridun** **Gregory Krumdick (PI)**

Project ID: ES167

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Washington, D.C.

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start date: Oct. 2010
- Project end date: Sept. 2017
- Percent complete: on going

Budget

- Total project funding:
  - $1.2M in FY16
  - $1.1M in FY17

Barriers

- Cost: Reduce manufacturing costs with advanced, continuous processing methods
- Performance: Optimization of particle structure and composition combination for maximum gradient material performance

Partners

- Active material process R&D:
  - Argonne's Applied R&D Group
    - Material synthesis and scale-up
  - University of Illinois at Chicago
    - 3D elemental mapping
  - Technische Universität Braunschweig
    - Particle stress study
  - Brookhaven National Laboratory, EES, Dr. Xiao-Qing Yang's group
    - Thermal stability
  - Laminar
    - Taylor Vortex Reactor process scale-up

Objectives - Relevance

- The objective of this program is to carry out a systematic research to:
  - Synthesize and evaluate various types of concentrated gradient cathode materials targeting ***> 220 mAh/g with > 95% capacity retention*** after 100 cycles.
  - Develop cost-effective batch and ***continuous processes*** for the scale-up of concentrated gradient cathode materials.
  - Provide ***sufficient quantities*** of these materials produced under rigorous quality control specifications for industrial evaluation of further research.

- The relevance of this program to the DOE Vehicle Technologies Program is:
  - The program is a key missing link between discovery of advanced battery materials, market evaluation of these materials and high-volume manufacturing.
    - Reducing the risk associated with the commercialization of new battery materials.
  - This program provides large quantities of materials with consistent quality.
    - For industrial validation in large format prototype cells.
    - For further research on concentrated gradient cathode materials.

Milestones

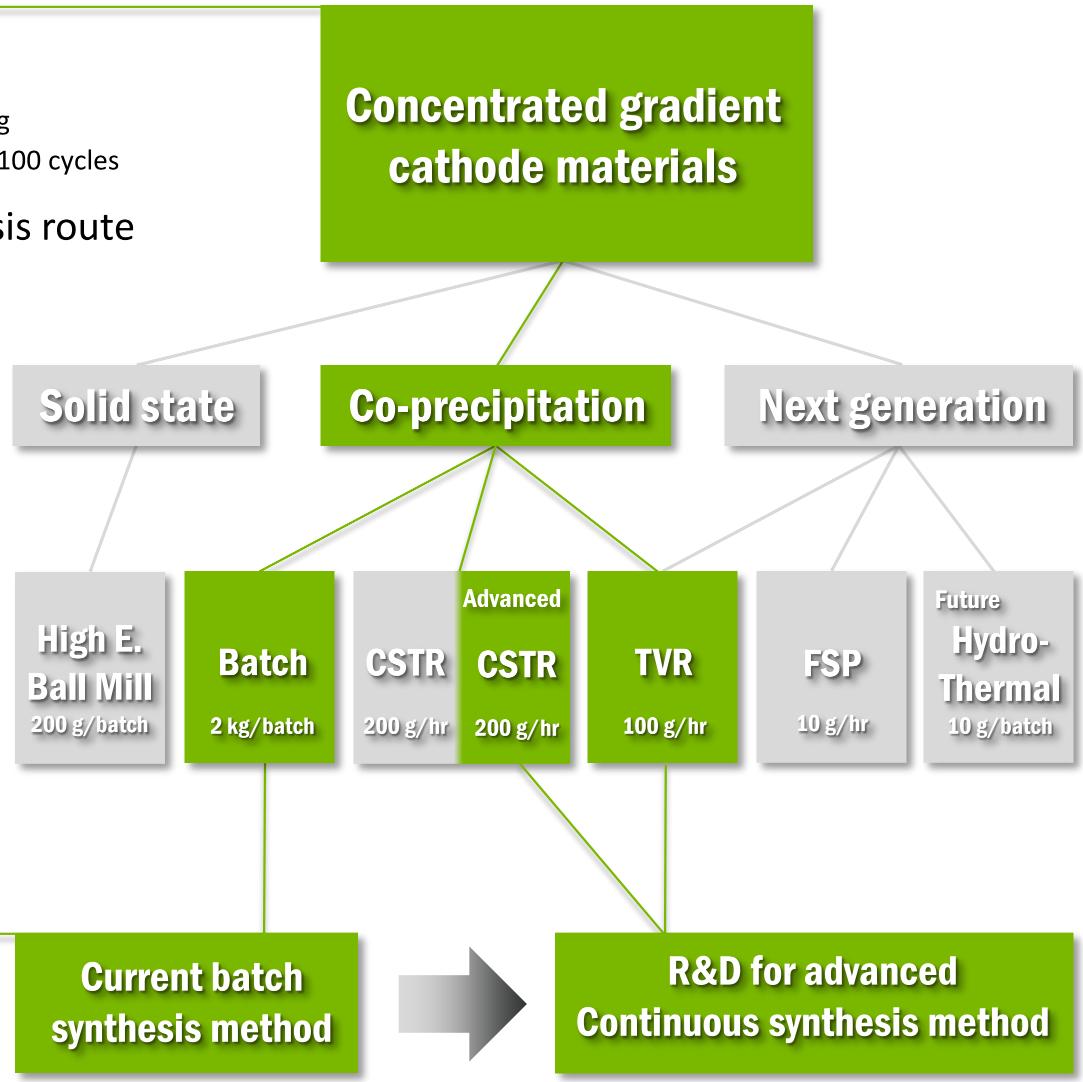
FY16	*Material*	Characterize preliminary 622 Gradient material	*Completed*	Q4
	Material	Deliver preliminary 622 Gradient material to BNL	*Completed*	
		− X-ray absorption spectroscopy		
FY17		− Thermal stability studies	*Completed*	Q1
	Material	Design high-capacity concentrated gradient materials	*Completed*	
		− 811 Gradient material ($LiNi_{\underline{0.90}}Mn_{0.05}Co_{0.05}O_2$ core + $LiNi_{\underline{0.33}}Mn_{0.33}Co_{0.33}O_2$ surface)		
		− 8 µm particle structure design (Core-Gradient & Core-Shell)		
	Process	Set up 20L batch reactor system for material synthesis	*Completed*	
	Material	Synthesize preliminary 811 Core-Gradient material	*Completed*	
	Material	Synthesize preliminary 811 Core-Shell material	*Completed*	
	Material	Characterize two prepared gradient materials	*Completed*	Q2
		− Cross-sectional mapping (SEM with EDS)		
		− Electrochemical test and comparison		
		− Thermal stability studies	Planned	Q3
	Material	Kg production of 811 Core-Shell and Core-Gradient materials	Planned	
	Material	Design other types of concentrated gradient materials such as FCG* and TSFCG**	Planned	
	Process	Investigate an advanced continuous synthesis process using 10L TVR***	Planned	

* Full Concentration-Gradient ** Two Slope Full Concentration-Gradient *** Taylor Vortex Reactor

Approach - Strategy

Material Synthesis and Evaluation

- Define target active material
  - Concentrated gradient cathode materials targeting
    > 220 mAh/g with > 95% capacity retention after 100 cycles
- Select synthesis process and synthesis route
  - Current: Batch process with hydroxide route
  - Future: Advanced continuous TVR process
- Produce preliminary materials
  - Gram scale preliminary synthesis of various types of concentrated gradient materials
  - Performance check for Go/No-Go decision
- Investigate particle structure and composition combination
- Production and distribution
  - 1 ~ 10 kilogram scale production
  - Characterization & pouch cell evaluation
  - Material support to assist other DOE programs



Process R&D for Scale-up

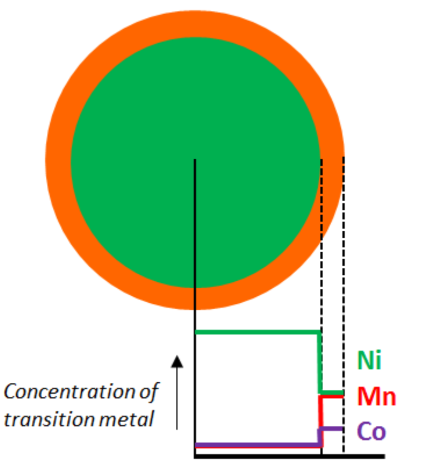
- Current 40L batch process
- Future continuous process

Gradient Material Strategy

❑ Gradient material will have the best of Core and Surface compositions

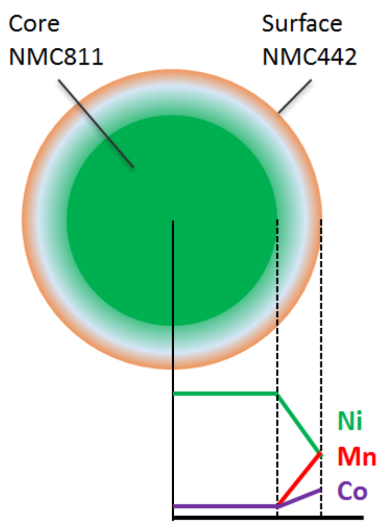
Core composition	- Ni-rich material : high capacity, low stability
Gradient layer	- Gradient layer : prevents the crack and segregation between Core and Shell
Surface composition	- Mn-rich material : low capacity, high stability

[*GEN 1*] Core-Shell



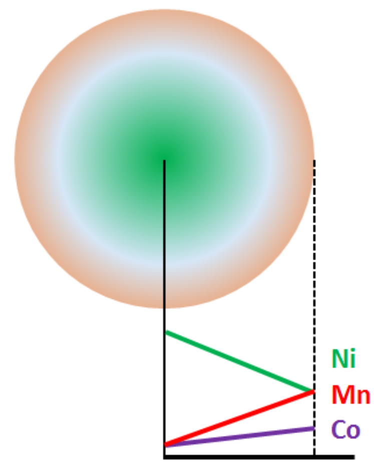
High capacity
Low particle strength
Low stability

[*GEN 2*] Core-Gradient (FY16)



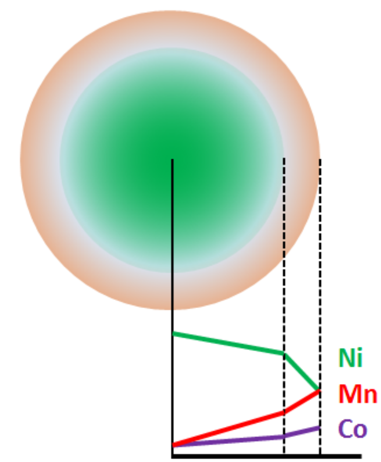
Medium capacity
Medium particle strength
Medium stability

[*GEN 3*] Full Concentration-Gradient



Low capacity
High particle strength
High stability

[*GEN 4*] Two Slope Full Concentration-Gradient



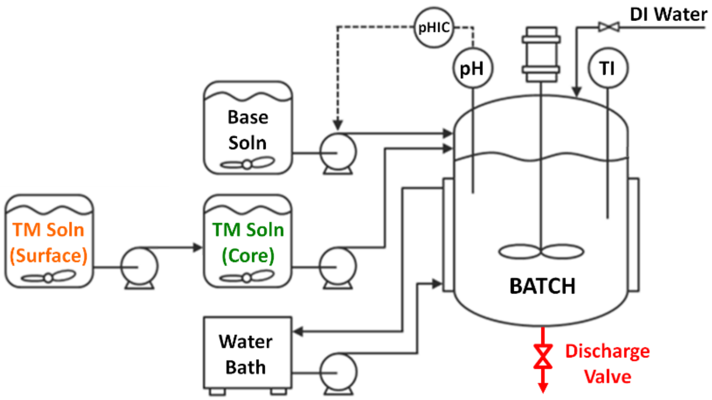
Medium capacity
High particle strength
High stability

Research target

1. Higher capacity - increase Ni portion
2. Higher particle strength – particle structure optimization
3. Higher stability – composition optimization

Gradient Material Synthesis Process

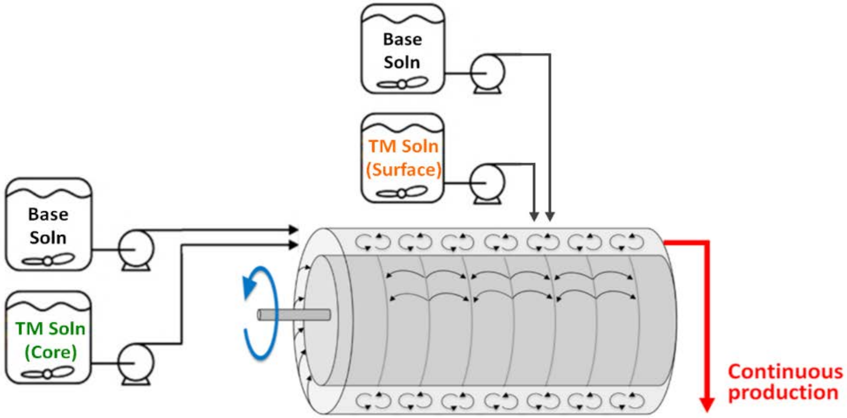
- Batch reactor system was used for gradient material synthesis **_Current batch production_**



*** First, Core TM solution feeding to batch reactor
Then, Surface TM solution feeding to Core TM solution tank**

✓ **Core TM solution changes to Surface TM solution gradually**

- Continuous production of gradient material is being investigated using Taylor vortex reactor system **_Process development for continuous production_**



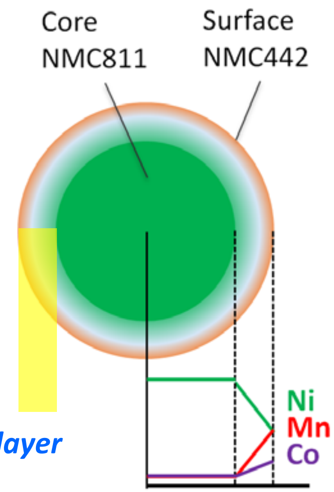
✓ **Surface TM solution is injected to the middle point of TVR**

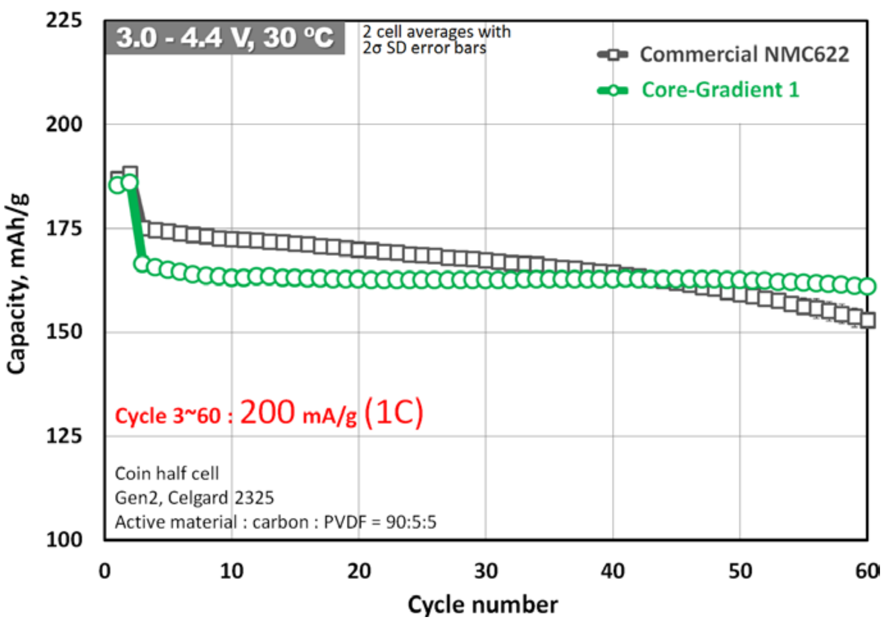
10 L Taylor Vortex Reactor in place

622 Gradient Material (FY16)

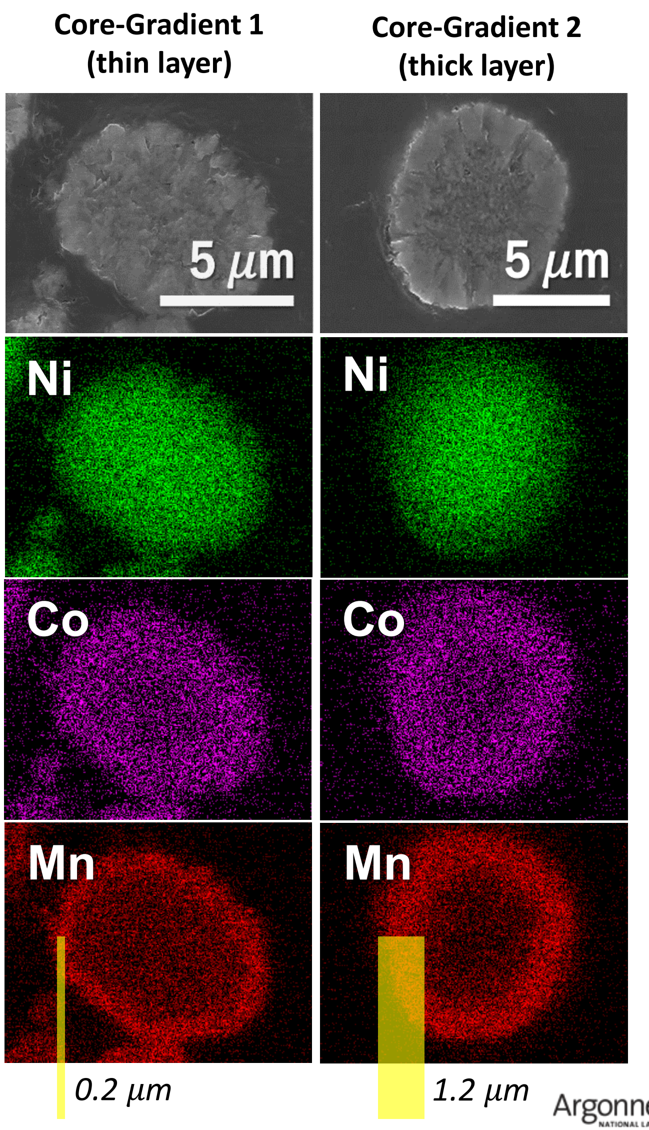
- Synthesis of 622 Gradient materials

  - Core-Gradient material was prepared and compared to a commercial NMC622 cathode.



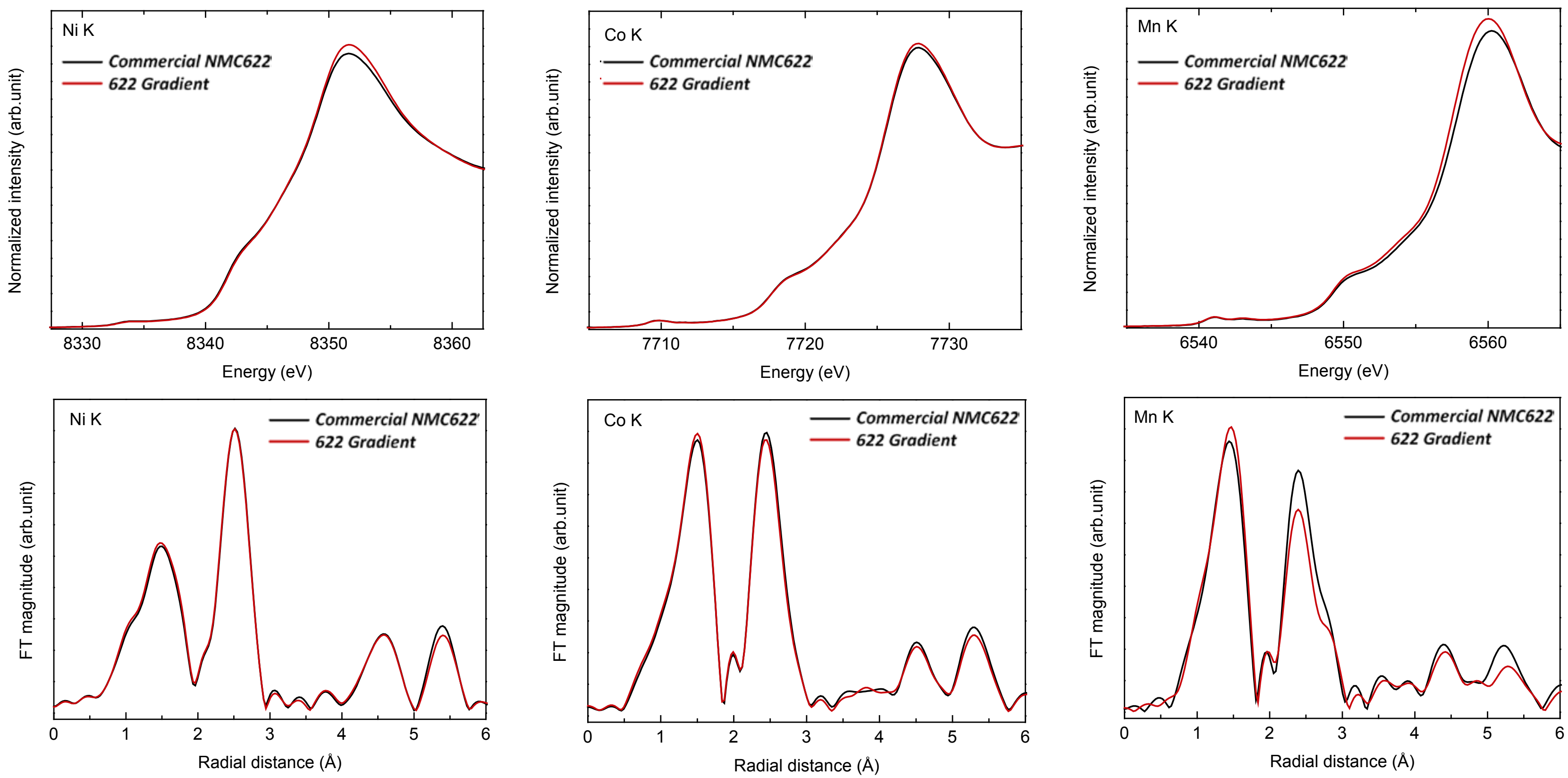


- Elemental mappings



622 Gradient Material Characterization

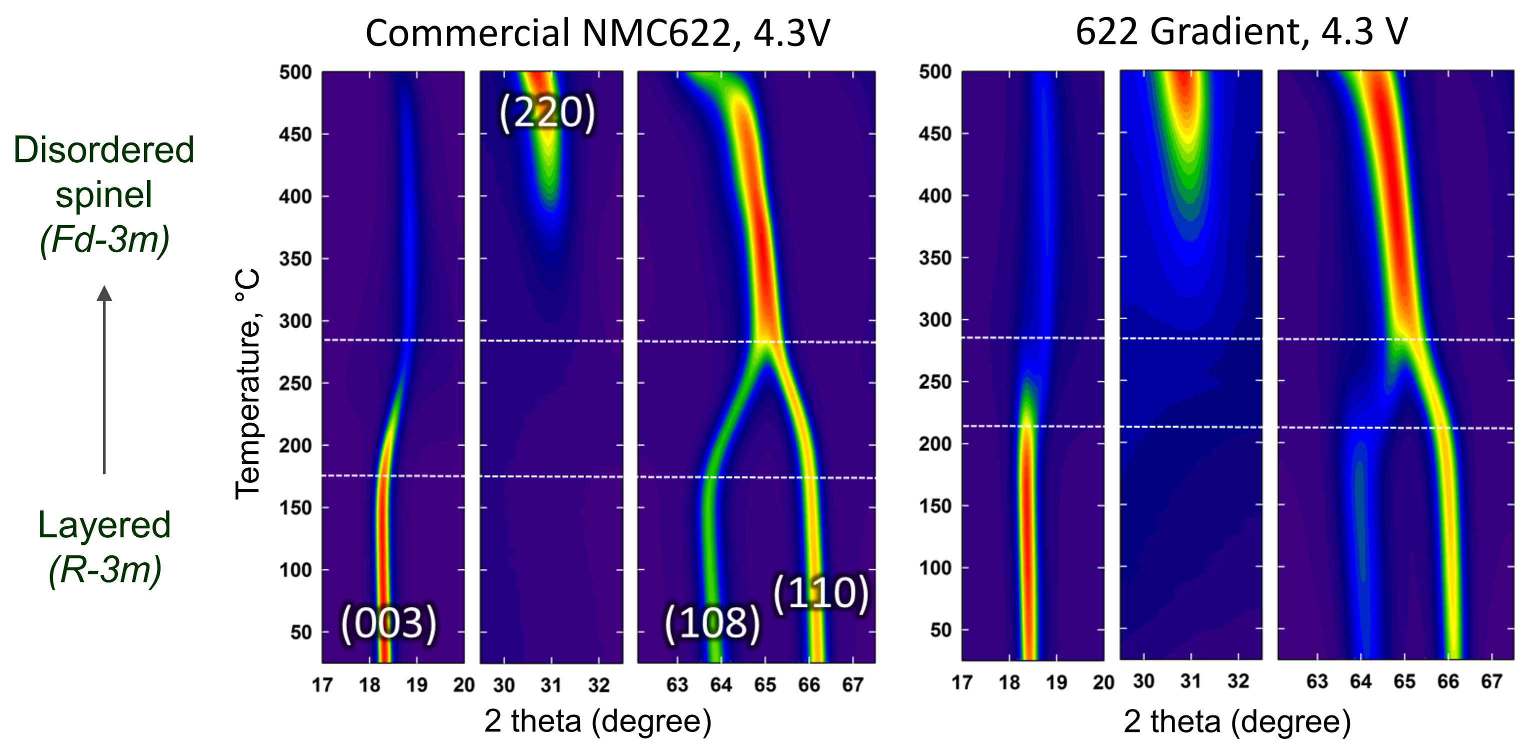
- X-ray absorption spectroscopy on commercial NMC622 and 622 Gradient materials
  (BNL, EES, Dr. Xiao-Qing Yang's group)



- ✓ *The Ni, Co and Mn K-edge XANES data are almost identical, which indicates that the average oxidation states of Ni, Co and Mn in commercial NMC622 and 622 Gradient cathodes are same.*
- ✓ *The local structure of Ni and Co are same. But Mn-M (M=Ni, Co, Mn) correlation at ~2.5 A shows a difference. The local structural analysis near surface by using soft X-ray and TEM will be conducted.*

622 Gradient Material Characterization

- Thermal stability studies on the charged 622 Gradient using time resolved XRD
  (BNL, EES, Dr. Xiao-Qing Yang's group)



✓ *The first phase transition from layered to spinel started at 175°C for commercial NMC622 while 622 Gradient shows the phase transition from at about 200°C.*

✓ *Peak broadening at charged state for 622 Gradient indicates the structural inhomogeneity characteristic.*

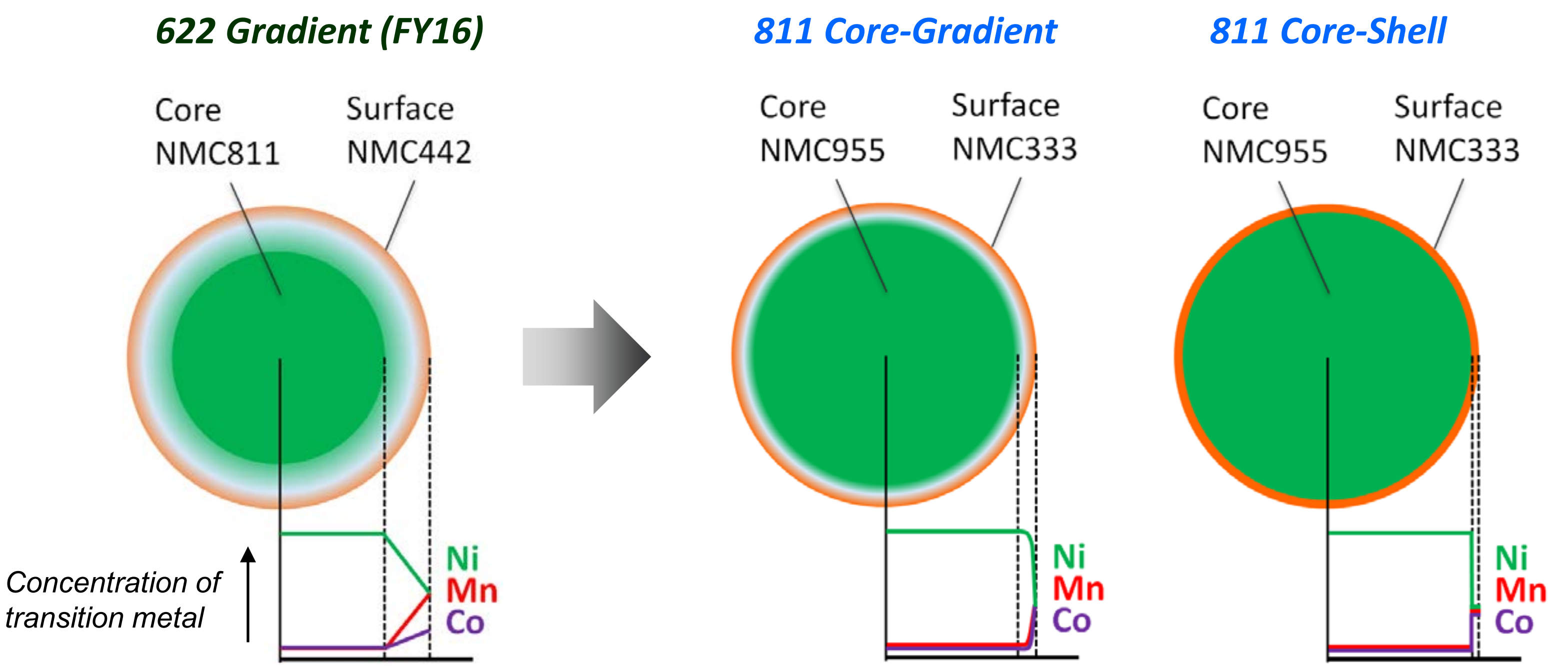
✓ *The gas analyze will be conducted to investigate the difference in (003) peak shift behavior.*

811 Gradient Material Synthesis

- To achieve higher-capacity gradient material with better cycle life

  1. **Core composition – $LiNi_{\underline{0.90}}Mn_{0.05}Co_{0.05}O_2$ for higher capacity**
  2. **Surface composition – $LiNi_{\underline{0.33}}Mn_{0.33}Co_{0.33}O_2$ for better stability**
  3. **Overall composition – $LiNi_{\underline{0.80}}Mn_{0.10}Co_{0.10}O_2$**

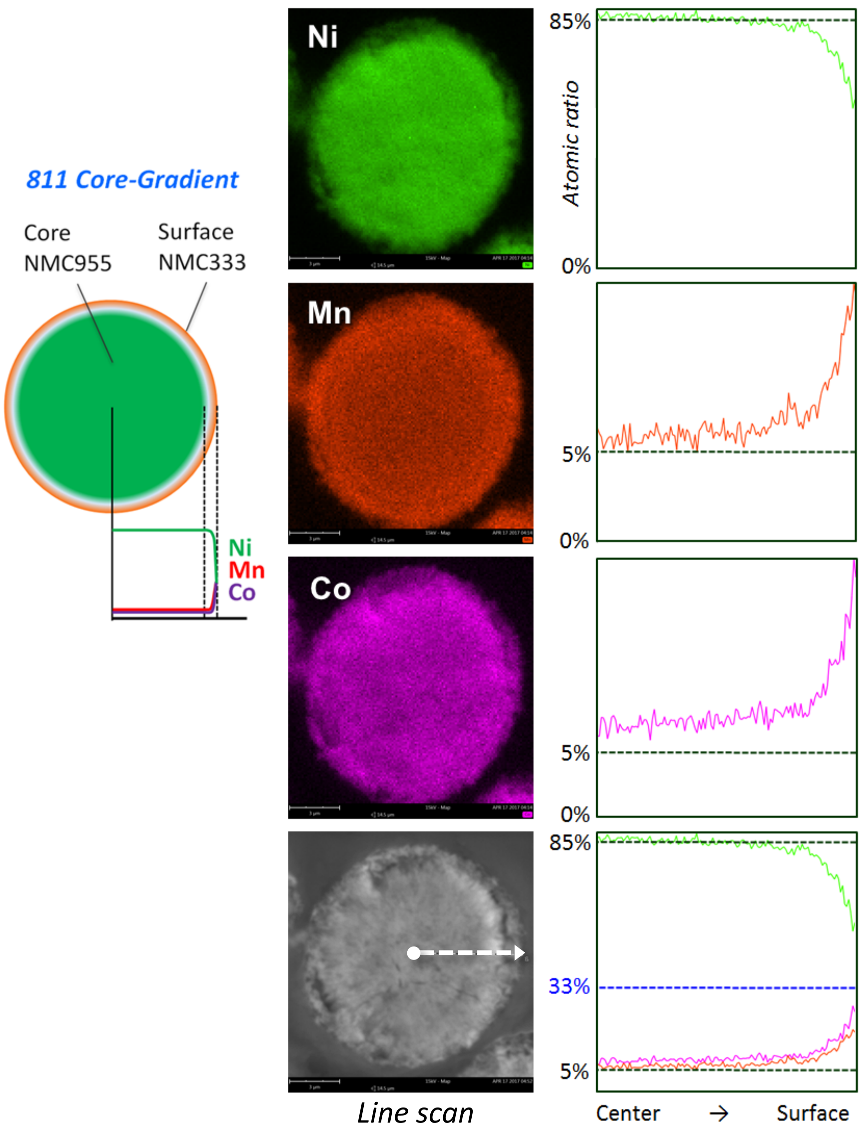
- Particle structure design for 811 Gradient materials

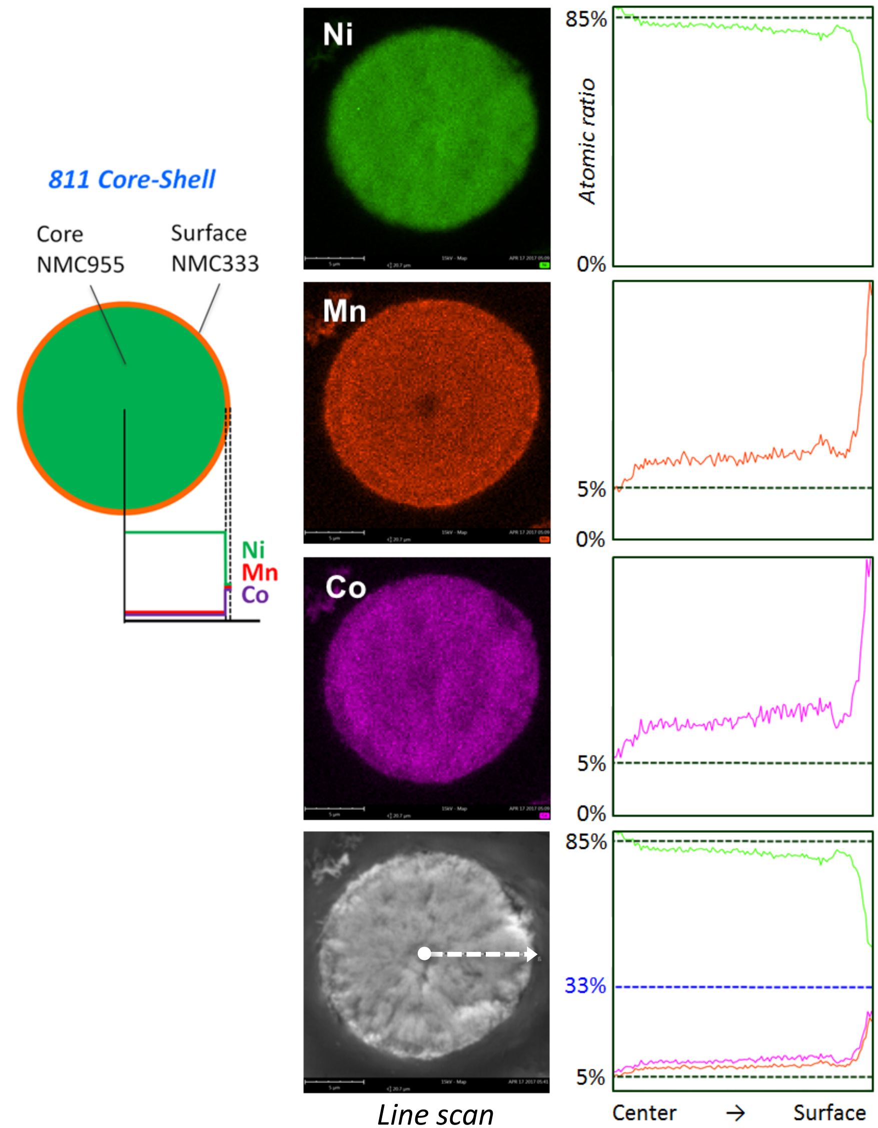


622 Gradient (FY16)	811 Core-Gradient	811 Core-Shell
Medium capacity	High capacity	High capacity
Medium particle strength	Medium particle strength	Low particle strength
Medium stability	Improved stability	Improved stability

811 Gradient Material Synthesis

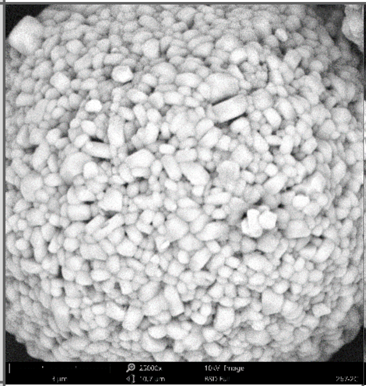
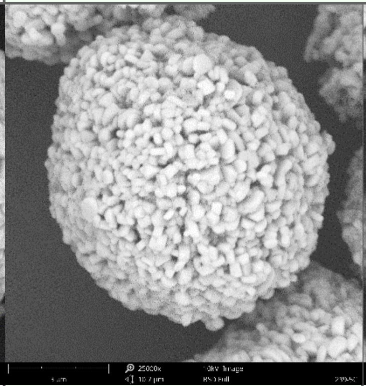
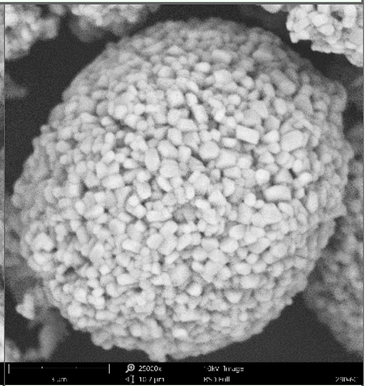
- SEM with EDS on synthesized 811 Gradient materials





Commercial NMC and 811 Gradient Materials

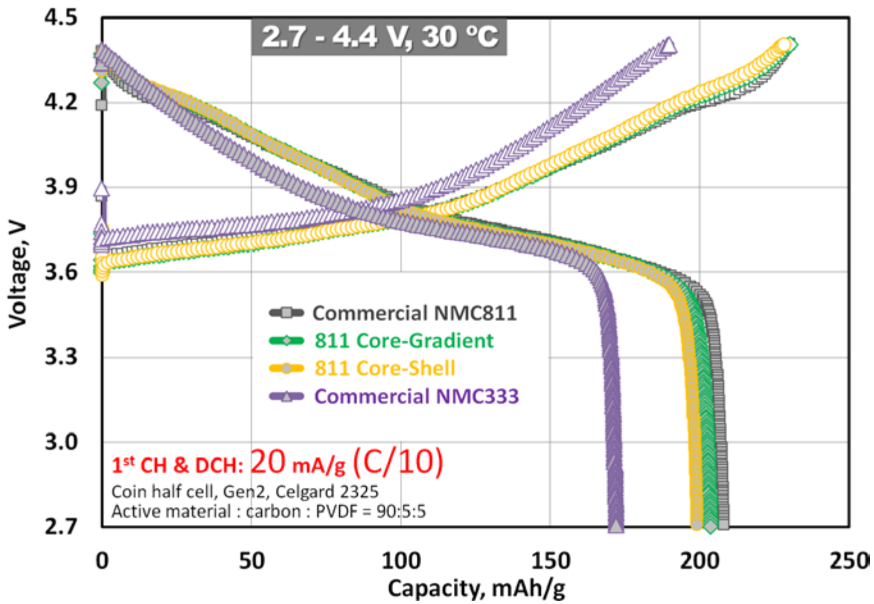
- Comparison of 811 Gradient material prepared using batch reactor

Material	NMC 811	NMC 333	811 Core-Gradient	811 Core-Shell
Scale / status	Commercial product		MERF pre-pilot preliminary product	
SEM				
Composition	NMC 811	NMC 333	~ NMC 811	~ NMC 811
ICP-MS analysis	$Li_{1.04}Ni_{\mathbf{0.80}}Mn_{0.10}Co_{0.10}O_y$	$Li_{1.07}Ni_{\mathbf{0.34}}Mn_{0.33}Co_{0.33}O_y$	$Li_{1.00}Ni_{\mathbf{0.76}}Mn_{0.12}Co_{0.12}O_y$	$Li_{1.00}Ni_{\mathbf{0.76}}Mn_{0.12}Co_{0.12}O_y$
Particle size D_{50} [µm]	13.7	11.7	8.0	8.0
BET [m^2/g]	0.37	0.34	0.55	0.57
* FCE [%]	90.0	90.5	88.1	86.7
* Avg. working voltage	3.86	3.88	3.87	3.87
* Discharge capacity @ 5 cycle [mAh/g]	**210.0**	**171.6**	**209.1**	**205.4**

* At C/10, 2.7 – 4.4 V and 30˚C

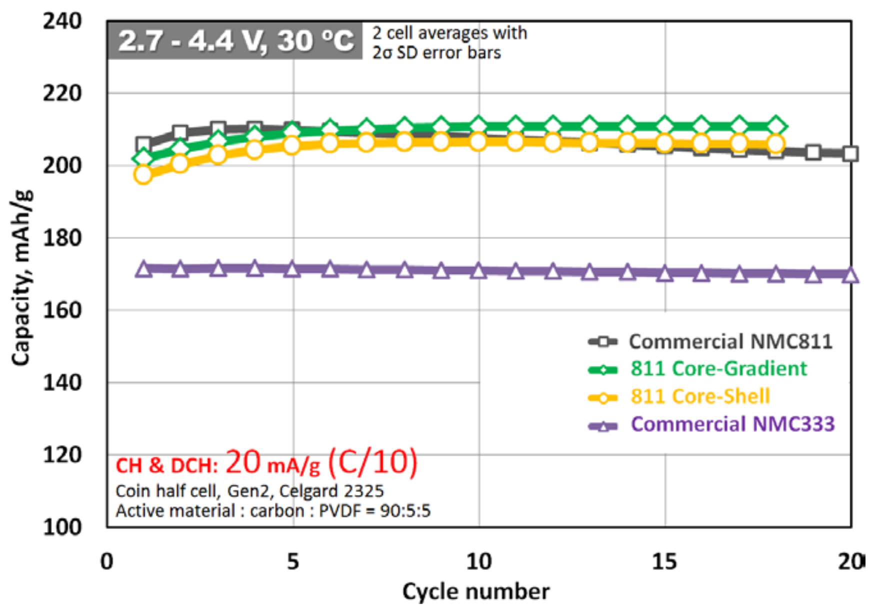
✓ *Gradient materials show reasonable physical electrochemical properties compared to a commercial NMC811.*

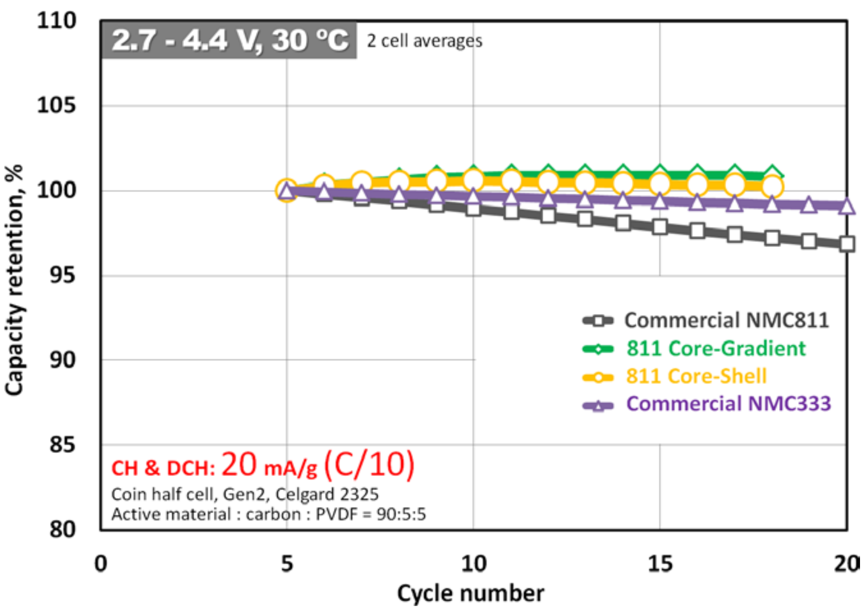
30°C Voltage Profile and C/10 Cycling



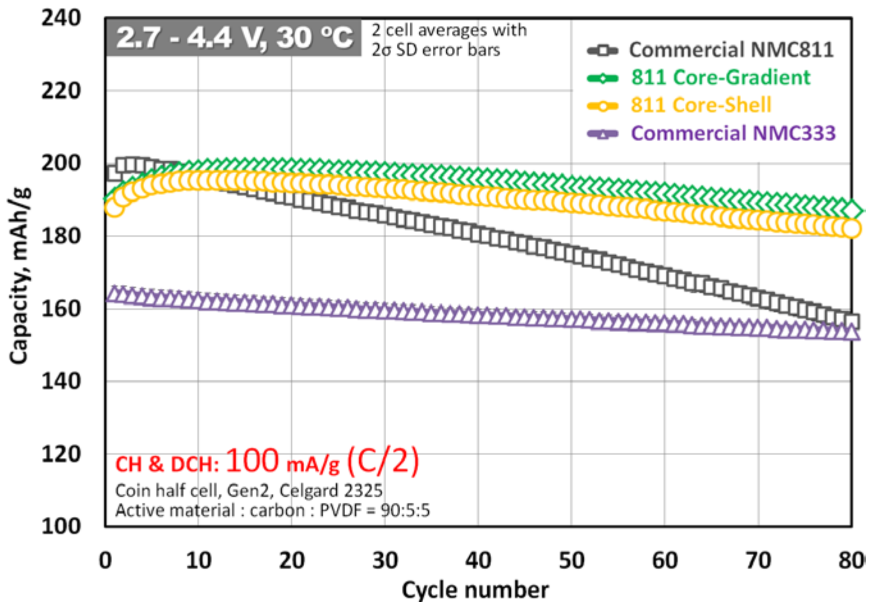
✓ *Both Core-Gradient and Core-Shell show high initial discharge capacity of 210 mAh/g at C/10 and 30°C.*

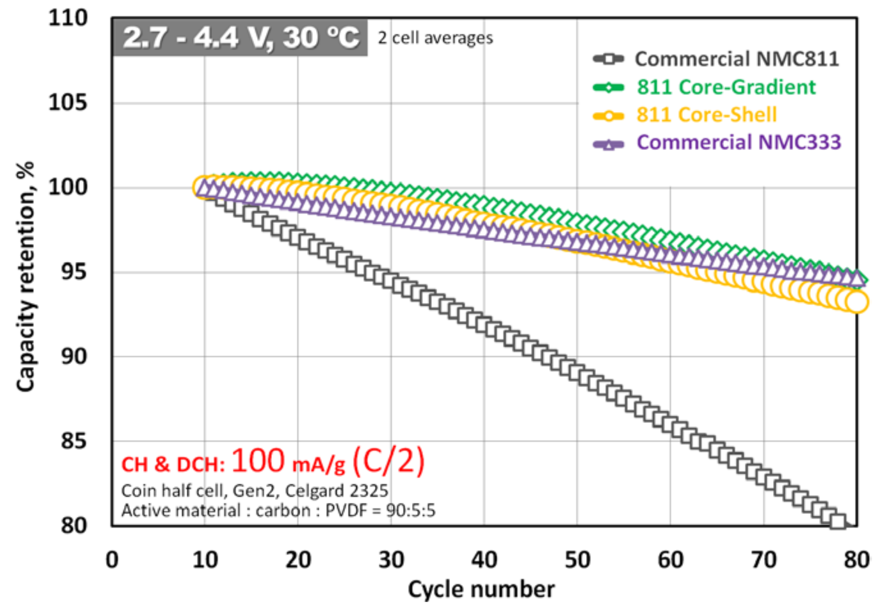
✓ *Gradient materials show improved capacity retention compared to commercial NMC811 and NMC333 at C/10 and 30°C.*

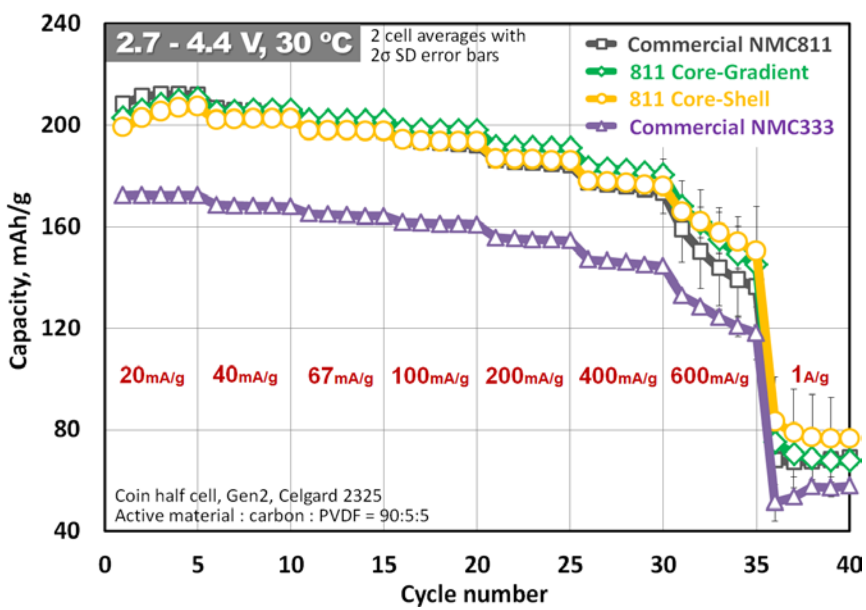


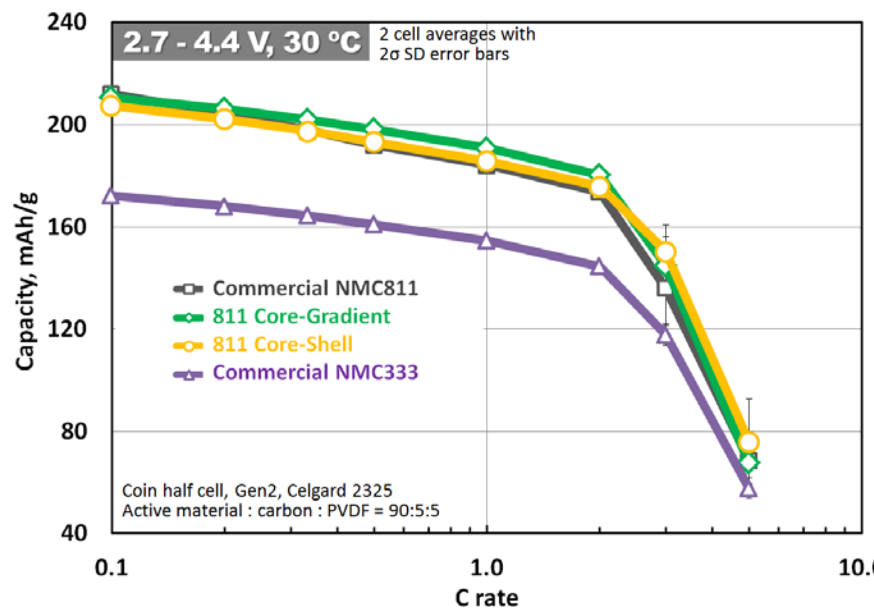


30°C C/2 Cycling and Rate Performance



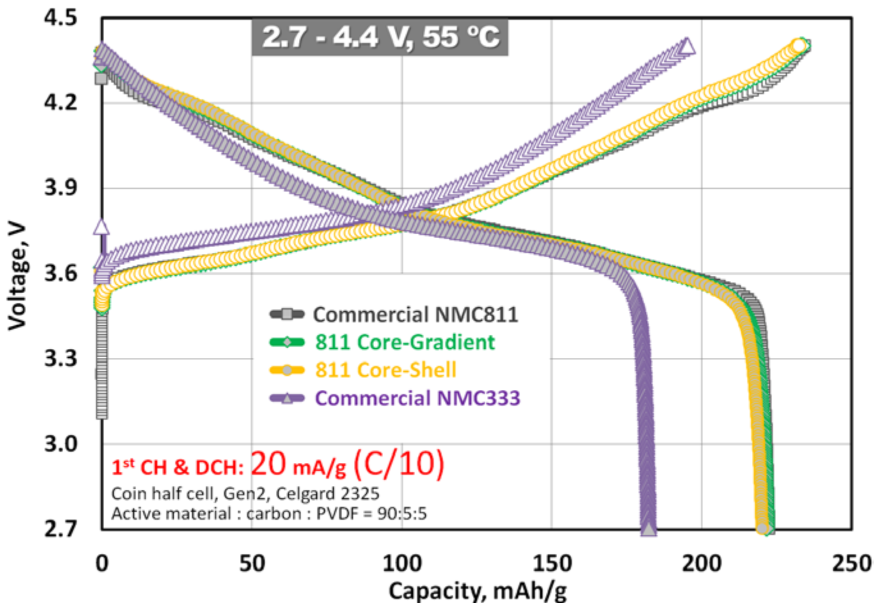




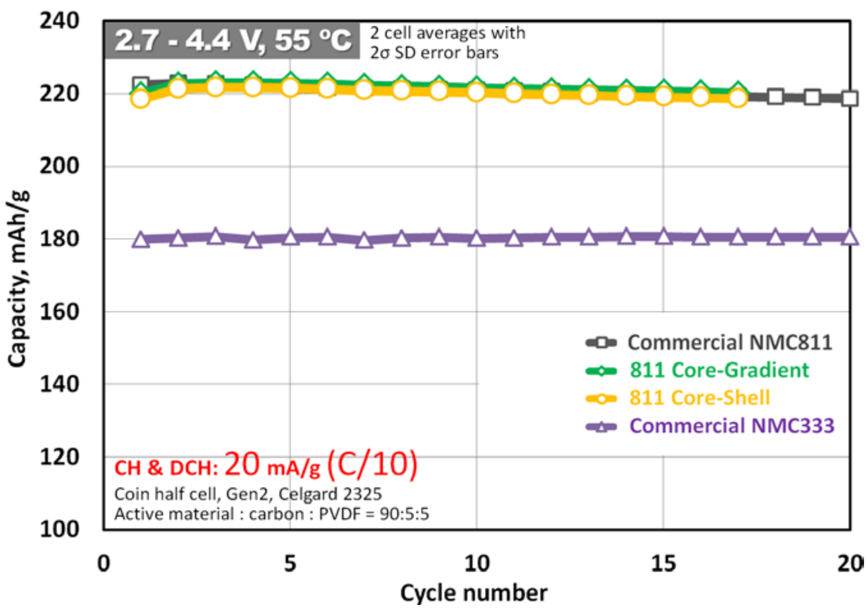


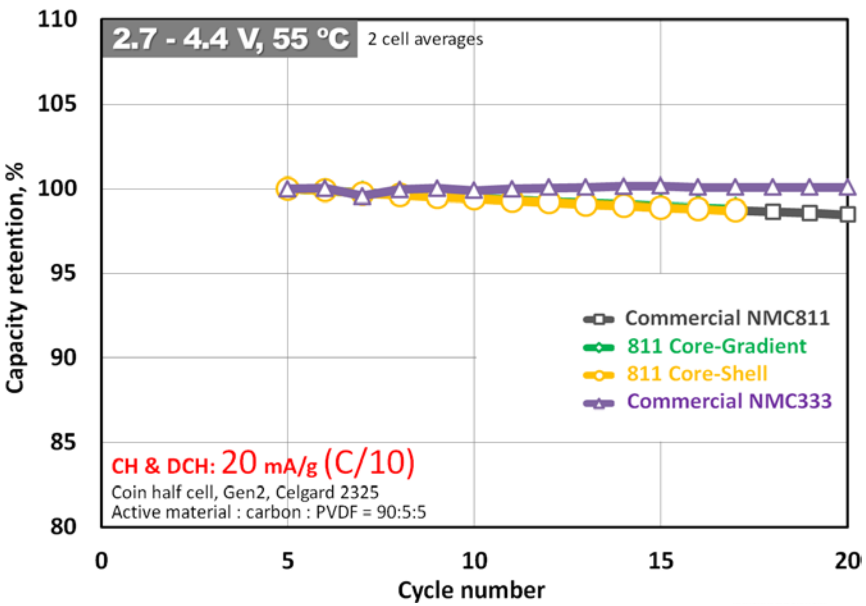
Technical Accomplishments

55°C Voltage Profile and C/10 Cycling



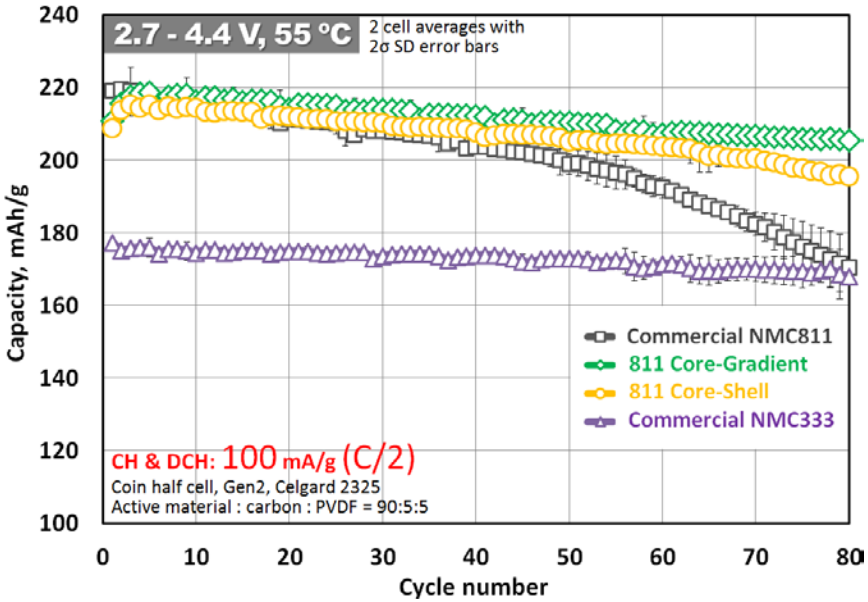
- ✓ *Both Core-Gradient and Core-Shell show high initial discharge capacity of 220 mAh/g at C/10 and 55°C.*
- ✓ *Gradient materials show similar capacity retention compared to commercial NMC811 at C/10 and 55°C.*

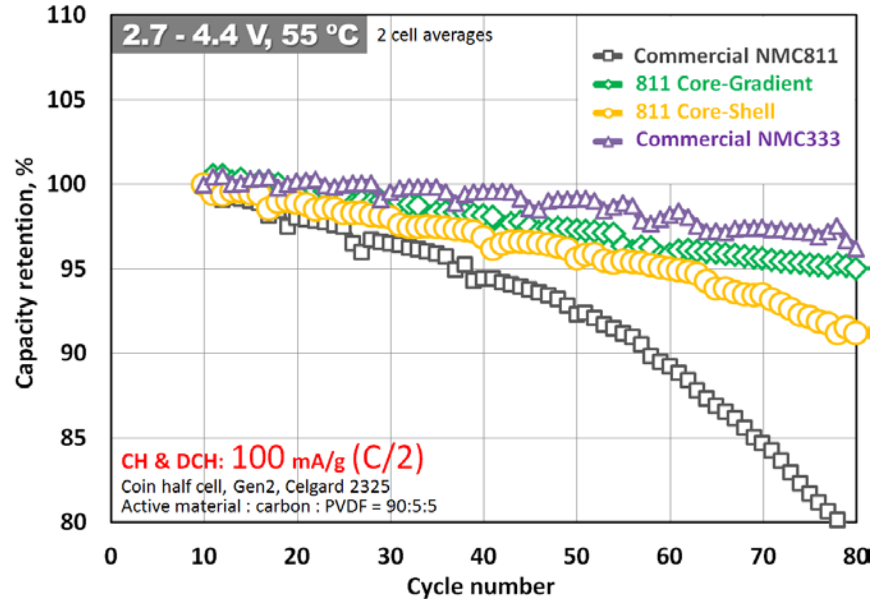


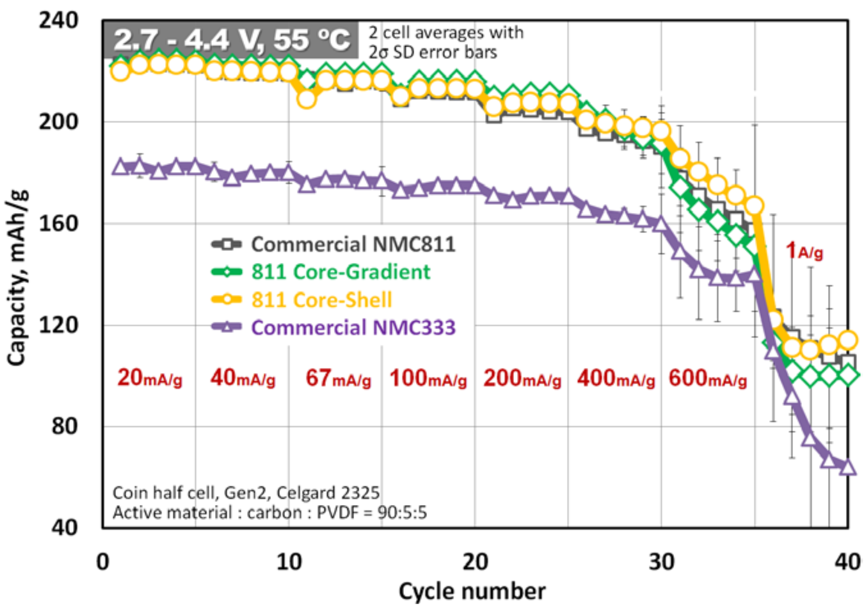


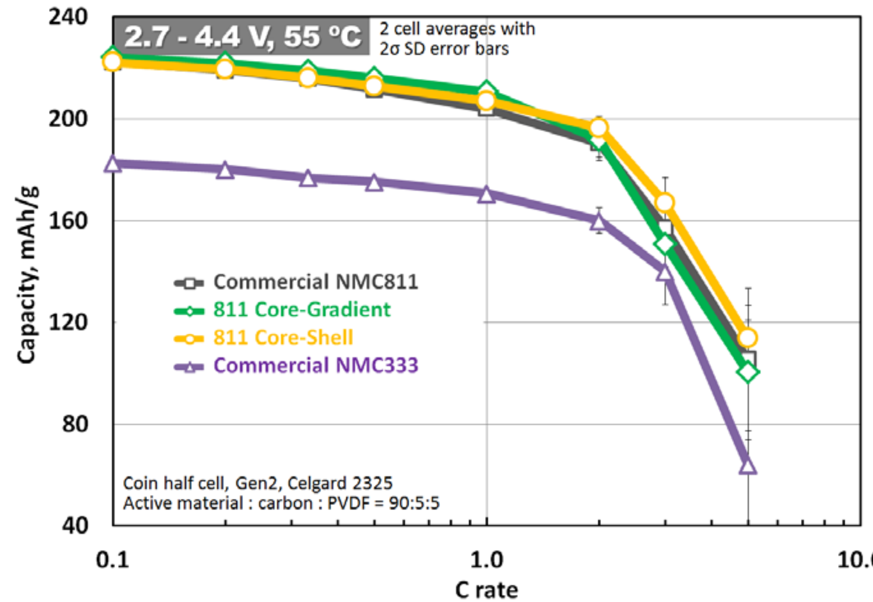
Technical Accomplishments

55°C C/2 Cycling and Rate Performance

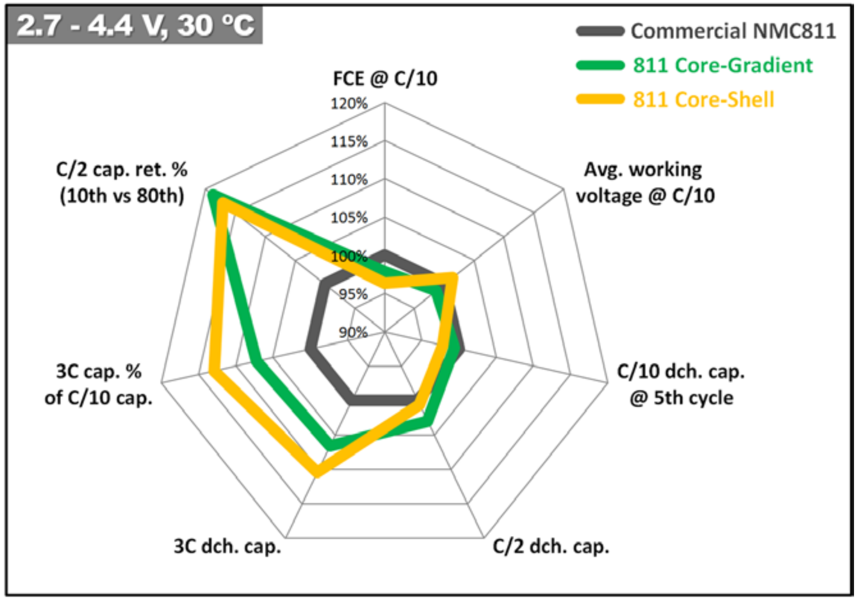




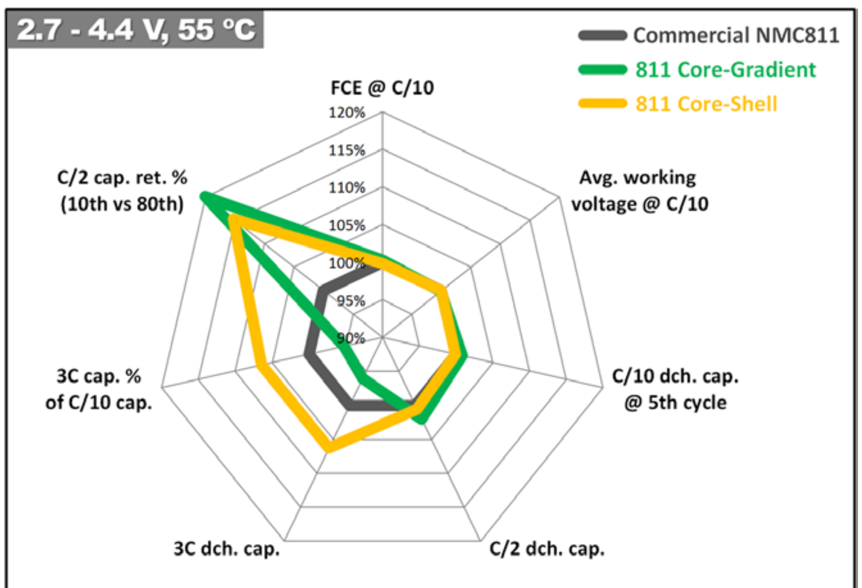


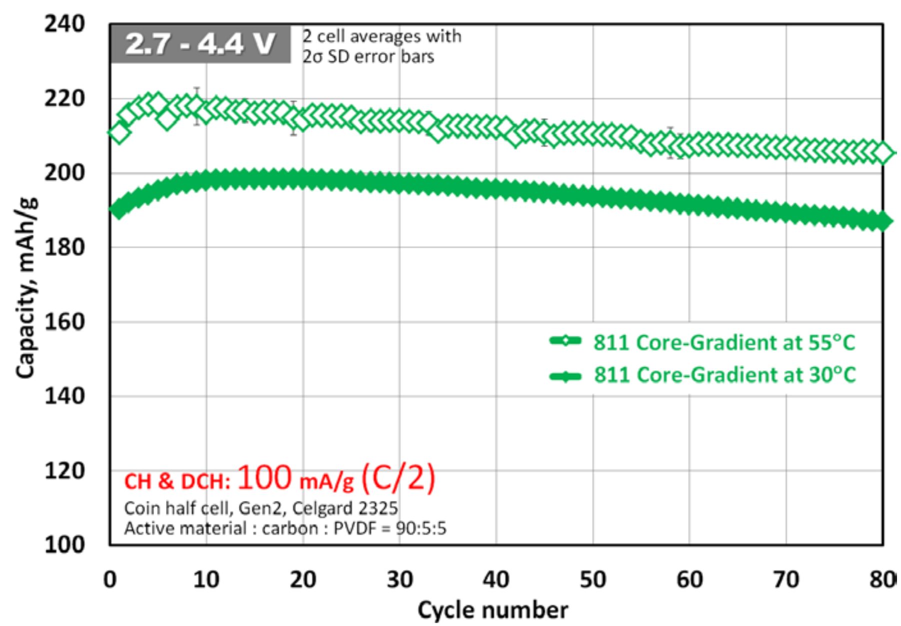


Radar Map Comparison and Conclusion



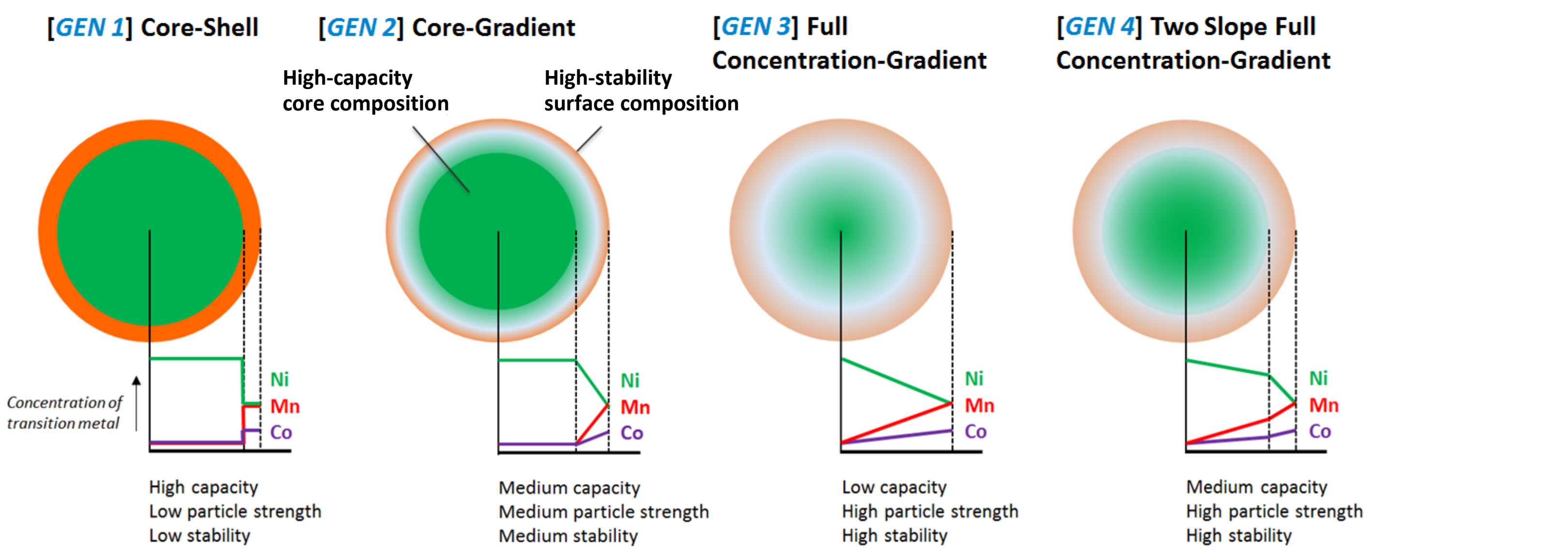
- ✓ *811 Core-gradient material shows 20% improved capacity retention compared to a commercial NMC811.*
- ✓ *811 Core-Shell material shows better rate capability.*
- ✓ *To further improve cycle life of NMC gradient materials, other additional approaches are necessary such as surface coating.*





Long-term Research Plan for Gradient Materials

- Investigate various particle structures and composition combinations
  - Particle strength analysis
  - 3D elemental mapping
  - Thermal stability



- Investigate an advanced continuous synthesis process
  - Advanced CSTR (Continuous Stirred Tank Reactor) system
  - TVR (Taylor Vortex Reactor) system
- Surface coating research on 811 Core-Gradient material to achieve improved cycle life

Responses to Previous Year Reviewers' Comments

- "The reviewer remarked outstanding performance meeting the needs of the industry and research community while adding value to ANL's thorough licensing strategies."
  - *Response:* *We will try to invent new types of concentrated gradient cathode material and develop its customized synthesis process which will generate several material and/or process patents to strengthen ANL's thorough licensing strategies.*

- "The reviewer said that the list of the collaborators demonstrated the trust this group has earned, well done. It will be interesting to see the performance of the commercialized products."
  - *Response:* *The characterization of the synthesized materials will be carried out in collaboration with several basic research groups for fundamental understanding. The physical and electrochemical properties of the synthesized 811 Core-Shell and Core-Gradient materials were compared to commercial NMC811 and NMC333. As such, newly prepared concentrated gradient cathodes will constantly be compared to an available commercial products with statistical evaluation.*

- "The reviewer commented that proposed future research is well-balanced to meet the program objectives and said highly qualified, hard-working team."
  - *Response:* *We will develop both new types of concentrated gradient cathode material and their new synthesis process which has economical feasibility with expertise and effort.*

Collaborations

- Material Characterization:
  - Brookhaven National Lab (Seongmin Bak)
    - Thermal stability
  - University of Illinois at Chicago (Jordi Cabana)
    - 3D elemental mapping
  - Technische Universität Braunschweig (Wolfgang Haselrieder)
    - Particle stress evaluation
- Synthesis process R&D:
  - Laminar Co., Ltd – CRADA
    - Taylor Vortex Reactor process scale-up
- Electrochemical evaluation of scaled materials:
  - Argonne's CAMP facility (Andrew Jansen)
- Thermal stability evaluation:
  - 622 Core-shell cathode to Brookhaven National Lab
  - 622 Core-gradient cathode to Brookhaven National Lab

Open to working with any group developing advanced active materials that will be beneficial for the ABR program.

Remaining Challenges and Barriers

- Development and scale-up of concentrated gradient cathode material is challenging but has great promise to improve the performance of battery materials.
- Continuous synthesis process for concentrated gradient cathode material need to be developed to lower manufacturing cost.
- Further improvement of concentrated gradient cathode material by surface coating is necessary to achieve longer cycle life.

Proposed Future Research

- **811 Core-Shell and Core-Gradient materials**
  - Kilogram scale-up of 811 Core-Shell and Core-Gradient materials (FY17)
  - Large format cell evaluation (FY17)
  - Thermal stability studies (FY17)
  - Surface coating studies to improve cycle life (FY17)
  - Particle strength analysis
  - 3D elemental mapping

- **Preliminary synthesis of other types of 811 concentrated gradient materials**
  - Investigate various particle structures such as FCG and TSFCG
  - Material characterization and comparison

- **Investigate an advanced continuous synthesis process**
  - Develop a customized continuous process for concentrated gradient materials

Any proposed future work is subject to change based on funding levels.

Summary

- **622 Gradient material characterization**
  - X-ray absorption spectroscopy
  - Thermal stability studies

- **811 Core-Shell and Core-Gradient materials**
  - Core ($LiNi_{\underline{0.90}}Mn_{0.05}Co_{0.05}O_2$) and surface ($LiNi_{\underline{0.33}}Mn_{0.33}Co_{0.33}O_2$) composition were determined
  - Particle structure (Core-Shell and Core-Gradient) was selected
  - 20L batch synthesis system was set up
  - Preliminary 811 Core-Shell material was synthesized
  - Preliminary 811 Core-Gradient material was synthesized
  - Cross-sectional mapping (SEM with EDS)
  - Electrochemical test and comparison to commercial products

- **Develop a customized continuous process**
  - Taylor Vortex Reactor system is being investigated

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  - Seongmin Bak
- Laminar
  - Jongpal Hong
- UIC
  - Jordi Cabana
- Technische Universität Braunschweig
  - Wolfgang Haselrieder